

ATMOS Measurements of $\text{H}_2\text{O}+2\text{CH}_4$ and Total Reactive Nitrogen in the November 1994 Antarctic Stratosphere: Dehydration and Denitrification in the Vortex

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Abstract. Simultaneous stratospheric volume mixing ratios (VMRs) of NO , NO_2 , HNO_3 , ClONO_2 , N_2O_5 , HO_2NO_2 , H_2O , CH_4 , and N_2O obtained inside and outside the Antarctic vortex from Atmospheric Trace Molecule Spectroscopy (ATMOS) solar occultation spectra recorded during 3-12 November 1994 reveal previously unobserved features in the distributions of total reactive nitrogen (NO_y) and total hydrogen ($\text{H}_2\text{O}+2\text{CH}_4$) during polar winter. Maximum removal of NO_y due to sedimentation of polar stratospheric clouds (PSCs) inside the vortex occurred at a potential temperature (θ) of 500-525 K (-20 km), where values were 5 times smaller than measurements outside. Maximum loss of $\text{H}_2\text{O}+2\text{CH}_4$ due to PSCs occurred in the vortex at 425-450 K, -3 km lower than the peak loss of NO_y . At that level, $\text{H}_2\text{O}+2\text{CH}_4$ VMRS inside the vortex were -70% of corresponding values outside. The Antarctic and April 1993 Arctic measurements by ATMOS show no significant differences in $\text{H}_2\text{O}+2\text{CH}_4$ VMRS outside the vortices in the two hemispheres.

Introduction

A primary objective of the ATLAS-3 shuttle mission from 3-12 November 1994, was to obtain profiles at high southern latitudes of stratospheric constituents involved in polar O_3 chemistry. During this mission, the ATMOS Fourier transform

spectrometer recorded 0.01-cm^{-1} resolution infrared solar spectra during 94 occultations near or over Antarctica. These spectra have been analyzed to derive profiles of ~ 30 molecules inside and outside the Antarctic vortex, which remained intact in the lower stratosphere with very low O_3 levels [Gunson et al. 1996; Manney et al., 1996]. Minimum Antarctic stratospheric temperatures of -200 K and the absence of strong, broad features in the spectra (except for known molecular bands) imply that polar stratospheric clouds (PSCs) had evaporated prior to the mission.

We report here an initial analysis of simultaneous VMR profiles of total reactive nitrogen, NO_y , and the sum of $\text{H}_2\text{O} + 2\text{CH}_4$ (total hydrogen less H_2), as a function of pressure and $[\text{N}_2\text{O}]$ (where $[x]$ denotes the VMR of species x). The cold temperatures inside the Antarctic vortex during austral winter promote the condensation of PSCs that provide surfaces for the heterogeneous activation of reactive chlorine and bromine, leading to catalytic destruction of O_3 in sunlit regions [cf. World Meteorological Organization (WMO), 1990]. Wide-spread, permanent removal of significant amounts of NO_y (denitrification) and H_2O (dehydration) by sedimentation of PSCs is a regular feature of the Antarctic vortex, but occurs less often and on smaller spatial scales in the Arctic vortex limiting losses of O_3 in the northern hemisphere [e.g. Fahey et al., 1990a]. Previous observations have suggested that the spread of denitrification and dehydration by mass flow from the Antarctic vortex affects the distribution of $[\text{NO}_y]$ and $[\text{H}_2\text{O}]$ over broad regions of the mid-latitude southern hemisphere [Kelly et al., 1989, 1990; Harwood et al., 1993; Pierce et al., 1994; Tuck et al., 1994]. We report ATMOS measurements over a wide altitude range inside and outside the vortex, revealing previously unobserved features in the distributions of $[\text{NO}_y]$ and $[\text{H}_2\text{O}] + 2[\text{CH}_4]$.

Measurements

The ATMOS measurements analyzed here were obtained with filter 3 (1580-3420 cm^{-1}) or 9 (650-2450 cm^{-1}) during sunrise occultations at. 64.5°S to 72.4°S latitude. Simultaneous H_2O , CH_4 , and N_2O profiles were derived from 25 filter 3 and 14 filter 9 occultations. Only filter 9 occultations measured all the gases used to define NO_y , calculated from $[\text{NO}_y] = [\text{NO}] + [\text{NO}_2] + [\text{HNO}_3] + 2[\text{N}_2\text{O}_5] + [\text{HO}_2\text{NO}_2] + [\text{ClONO}_2]$.

Version 2 profiles are presented here with no diurnal corrections applied to the retrievals of NO and NO_2 [Gunson et al., 1996]. Photochemical model studies have shown that differences between $[\text{NO}] + [\text{NO}_2]$ obtained with and without diurnal correction factors are <0.2 ppbv (10^{-9} by volume) for a wide range of conditions in the lower stratosphere [Newchurch et al., 1996], producing a negligible error in $[\text{NO}_y]$. Additionally, $[\text{NO}_y]$ was calculated assuming a 3-km scale height decreases in $[\text{N}_2\text{O}_5]$, $[\text{ClONO}_2]$, $[\text{HO}_2\text{NO}_2]$, $[\text{NO}]$, and $[\text{HNO}_3]$ above and below the altitude range of the measurements. Our determination of NO_y is not sensitive to this assumption because the extrapolated VMKS are small relative to those of the measured species. ATMOS and correlative ER-2 measurements of NO_y , H_2O , and CH_4 show excellent agreement suggesting the true systematic error in the ATMOS measurements of $[\text{NO}_y]$ may be less than the value of 10-15% estimated by combining the systematic uncertainties of the individual constituents [Chang et al., 1996].

Analysis

ATMOS Antarctic measurements of $[\text{H}_2\text{O}] + 2[\text{CH}_4]$ (denoted $[\text{H}]$), $[\text{H}_2\text{O}]$, and $[\text{NO}_y] - [\text{NO}_y^*]$ (denoted $[\text{AN}]$) are displayed versus θ and longitude in Fig. 1. Longitude is a useful coordinate since the measurements were obtained over a narrow latitude range and the vortex was at similar longitudes throughout the mission [Manney et al., 1996]. $[\text{NO}_y^*]$,

the NO_y VMR expected in the absence of denitrification, was derived from a fit to $[\text{NO}_y]$ versus $[\text{N}_2\text{O}]$ measured outside the vortex. Contours of $[\text{N}_2\text{O}]$ (overlayed) show the clear signature of deep descent between longitudes of $\sim 230^\circ\text{E}$ to 30°E .

Above 550 K, measurements of $[\text{H}]$ (top) are characterized by values between 7.0 and 7.5 ppmv (10⁻⁹ by volume), a small increase with θ , and no obvious longitude dependence despite differences of two orders of magnitude between $[\text{N}_2\text{O}]$ inside and outside the vortex near 700 K. Below 550 K, $[\text{H}]$ decreases sharply to a minimum of 4 ppmv in the vortex interior. Minimum $[\text{H}]$ and the corresponding θ agree with measurements from the Halogen Occultation Experiment. during September and October 1992 [Pierce et al., 1994].

The distribution of $[\text{H}_2\text{O}]$ (middle) is 1.5 ppmv higher inside the vortex than outside between 550 and 900 K, due to downward transport of moist. air from the upper stratosphere and lower mesosphere. Similar $[\text{H}_2\text{O}]$ observations in the November 1991 southern vortex were reported by Harwood et al. [1993]. Minimum $[\text{H}_2\text{O}]$ of 2 ppmv in the vortex is also consistent with previous measurements [Kelly et al., 1990; Pierce et al., 1994; Santee et al., 1995].

The ATMOS $[\text{AN}]$ measurement-s (bottom) reveal massive denitrification within the vortex between about 400 and 600 K. The signature of denitrification extends to extra-vortex air near 180°E for $\theta < 400$ K. However, the vast majority of extra-vortex air shows no significant denitrification. Enhanced $[\text{NO}_y]$ exists in the vortex between 700 and 900 K, for air characterized by exceedingly low $[\text{N}_2\text{O}]$.

Values of scaled potential vorticity (SPV) in 10^{-4} s^{-1} [Manney et al., 1996] were used to classify each measurement as inside the vortex ($\text{SPV} > 2$), outside ($\text{SPV} < 1$), or as intermediate "edge" air ($1 < \text{SPV} < 2$). $[\text{N}_2\text{O}]$ is well correlated with SPV values above 400 K; below this level, $[\text{N}_2\text{O}]$ is relatively well-mixed with respect to longitude, while SPV gradients for the same locations and times suggest that the vortex extended down at least to

375 K [Abrams et al. , 1996; Manney et al. , 1996] .

Figure 2 shows $[H]$ versus the \log of $[N_2O]$ for measurements between 320 and 2050 K. The solid line, a linear fit to the out-of-vortex measurements (filled circles), defines $[H^*]$ versus $[N_2O]$, the out-of-vortex reference relation. Values of $[H^*]$ decrease from 7.70 ppmv at 2 ppbv of N_2O to 7.00 ppmv at 300 ppbv of N_2O ; increases at low $[N_2O]$ are presumably due to the oxidation of H_2 . Values of $[H_2]$ inside the vortex (open circles) lie below the reference relation, especially for $[N_2O]$ between 20 and 250 ppbv. This difference defines the level of dehydration in the vortex since similar relations would be expected in both regions due to the long lifetimes of the gases and the absence of sedimentation by PSCs .

The dashed line in Fig. 2 shows a fit to ATMOS/ATLAS 2 Arctic extra-vortex ($sPV > 2$) $[H^*]$ measurements from filter 2 (1100-2000 cm^{-1}) and 3 (1580-3400 cm^{-1}). The observations were recorded between 8 April and 17 April 1993. Antarctic extra-vertical $[H^*]$ averages 0.2-0.3 ppmv higher than values in the Arctic for the same $[N_2O]$. In contrast., -1 ppmv lower $[H_2O]$ was measured outside the vortex in the Ant-arctic than in the Arctic from the ER-2 aircraft [Kelly et al., 1990; Fahey et al., 1990a] . The cause of this difference is not clear.

In Fig. 3, simultaneous ATMOS measurements of $[NO_y]$ and $[N_2O]$ in the Antarctic are shown. The filled circles ($sPV < 1$) define a compact out-of-vortex relation over the full measurement range. A least-squares fit to these measurements (solid curve) defines $[NO_y^*]$ vs. $[N_2O]$. The substantial change in the slope of the reference curve at low $[N_2O]$ reflects the upper atmospheric sink of NO_y due to the $NO + N$ loss reaction [Fahey et al., 1990b] . The dashed curve shows the average out-of-vortex relation derived equatorward of the vortex boundary from 1987 Ant-arctic and 1989 Arctic ER-2 in situ measurements [Fahey et al. , 1990a, Fig. 1] . Evidence for a nonlinear

correlation between $[\text{NO}_y]$ and $[\text{N}_2\text{O}]$, not due to denitrification, was reported during AASE II [Loewenstein et al., 1993, Fig. 3b], consistent with other NO_y measurements at low $[\text{N}_2\text{O}]$ [e.g., Fahey et al., 1990b; Kondo et al., 1994].

Measurements of $[\text{NO}_y]$ inside the vortex (open circles, plus symbols) in Fig. 3 diverge from the reference relation at $[\text{N}_2\text{O}] \approx 270$ ppbv. These differences define the extent of denitrification due to sedimentation of PSCs. The minimum $[\text{NO}_y]/[\text{NO}_y^*]$ ratio of 0.2 occurred at $[\text{N}_2\text{O}] \approx 100$ ppbv. The minimum $[\text{NO}_y]$ of -3 ppbv measured by ATMOS inside the vortex agrees with the lowest levels of ~ 11 ppbv measured in the Antarctic vortex during August, 1987 [Fahey et al., 1989].

Based on the ATLAS 3 measurements and the corresponding out-of-vortex reference curves in Figs. 2 and 3, $[\text{AH}]$, defined as $[\text{H}] - [\text{H}^*]$, and $[\text{AN}]$ have been calculated as a function of θ . Values for measurements with $\text{sPV} > 2$ (vortex interior air) are given in Table 1. The minimum $[\text{AH}]$ is reached at 425-450 K, ~ 17 km altitude, whereas the minimum $[\text{AN}]$ occurred at 500-525 K, ~ 20 km altitude.

The results in Table 1 indicate that the maximum NO_y removal occurred at a higher altitude than that of $\text{H}_2\text{O} + 2\text{CH}_4$. These results are consistent with Antarctic aircraft measurements which observed type I PSCs above the altitude range containing type II PSCs [Kinne et al., 1989]. The measured altitude distributions of NO_y and $\text{H}_2\text{O} + 2\text{CH}_4$ in Table 1 provide a unique observational constraint for understanding the microphysical processes that result in PSC formation, denitrification, and dehydration.

Antarctic PSCs are observed between altitudes of 14 and 28 km with a peak sighting frequency at ~ 19 km during austral late winter and early spring [Poole and Pitts, 1994]. The $[\text{AH}]$ and $[\text{AN}]$ changes with θ are roughly consistent with the observed PSC sighting frequency distribution below and near its peak altitude, but the variations above 575 K are not: $[\text{AH}]$ reaches a minimum at

600-700 K and [AN] is positive above 650 K with a maximum of +5.6 ppbv at 700-750 K, which correspond to the region of maximum descent indicated by [N₂O] (Fig. 1).

Large NO amounts produced in the lower thermosphere both by solar radiation during quiet times and through auroral ionization may reach the stratosphere, particularly in polar regions during winter when loss of NO_y shuts down due to cessation of photolysis of NO [Solomon et al., 1982]. We hypothesize that the positive [AN] values may have resulted from the descent of such air with elevated NO into the Antarctic vortex.

Aside from dehydration, [AH] is determined by the chemistry of CH₄ oxidation and the descent of air. Model calculations predict significant [H] variations in the upper stratosphere and lower mesosphere; in particular, high [H₂] and low [H₂O] are calculated for this region during high latitude winter [Le Texier et al., 1988]. We suggest that [AH] above -575 K may have resulted from the descent into the vortex of H₂O-poor/H₂-rich air produced in the lower mesosphere during winter. As temperatures below 1.95 K occurred up to -15 mbar during the 1994 Antarctic winter, dehydration and denitrification may also have played a role in determining [AH] and [AN] at the higher altitudes.

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Table 1. ATMOS Antarctic [ΔH] and [AN]
Measurements with sPV < 2.0 versus θ

θ (K)	[ΔH] (ppmv)	[AN] (ppbv)
750-800	-0.66(0.05)	3.21
700-750	-0.63(0.35)	5.84(0.24)
650-700	-0.46(0.25)	3.36(2.03)
600-650	-0.43(0.24)	-0.92(3.03)
575-600	-0.49(0.13)	-6.31(0.36)
550-575	-0.88(0.44)	-9.88(1.32)
525-550	-1.11(0.15)	-12.00
500-525	-1.75(0.41)	-13.07(0.63)
475-500	-1.81(0.29)	
450-475	-2.22(0.30)	-12.44(1.24)
425-450	-2.42(0.47)	-10.18(2.07)
400-425	-2.25(0.58)	-8.97(1.64)

Values in parentheses are standard
deviations.

Figure Captions

Fig. 1. Distributions of [H] (top) , [H₂O] (middle), and [AN] (bottom) versus θ and longitude ($^{\circ}$ E). Inverted triangles mark the longitudes of the measurements. Contours of [N₂O] (ppbv) are superimposed.

Fig. 2. ATMOS/ATLAS 3 [H] (ppbv) VS. [N₂O] (ppbv) from Antarctic measurements between θ of 320 K and 2050 K. The symbols show classifications based on SPV. A solid line shows the fit to the solid circle measurements (SPV<1). The dashed line shows the fit to ATMOS/ATLAS 2 Arctic measurements (not shown) with SPV<1. The lines are defined by $[H^*] = a + b \cdot \log_{10}[N_2O]$ with $a = 7800.6228$ and $b = -323.6982$ for the Antarctic and $a = -7478.1497$ and $b = -267.50353$ for the Arctic data.

Fig. 3. [NO_y] (ppbv) vs. [N₂O] (ppbv) from ATLAS 3 Antarctic filter 9 sunrise measurements with θ between 320 K and 2050 K. The solid curve defines the [AN] relation determined from a least-squares fit to the solid circles. The best-fit curve is given by $[NO_y^*] = a + bx + cx^2 + dx^3 + ex^4$ with $a = -1.3820071$, $b = 30.022251$, $c = -32.447532$, $d = 21.963289$, $e = -5570435.5$, and $x = \log_{10}[N_2O]$. The dashed curve shows the linear [NO_y*]-[N₂O] relation derived from Arctic and Antarctic ER-2 aircraft measurements by Fahey et al. [1990a].

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Figure 1

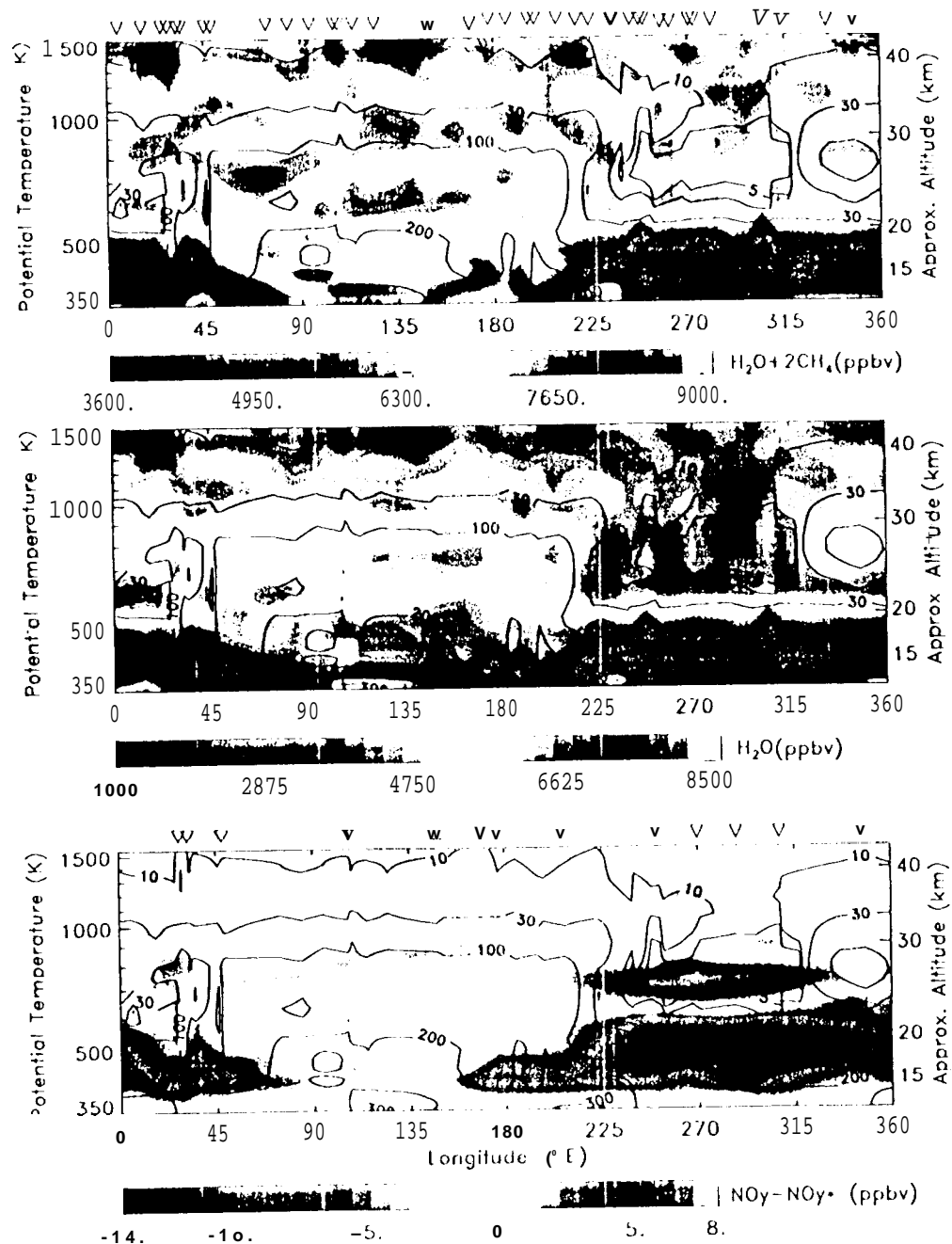


Figure 2

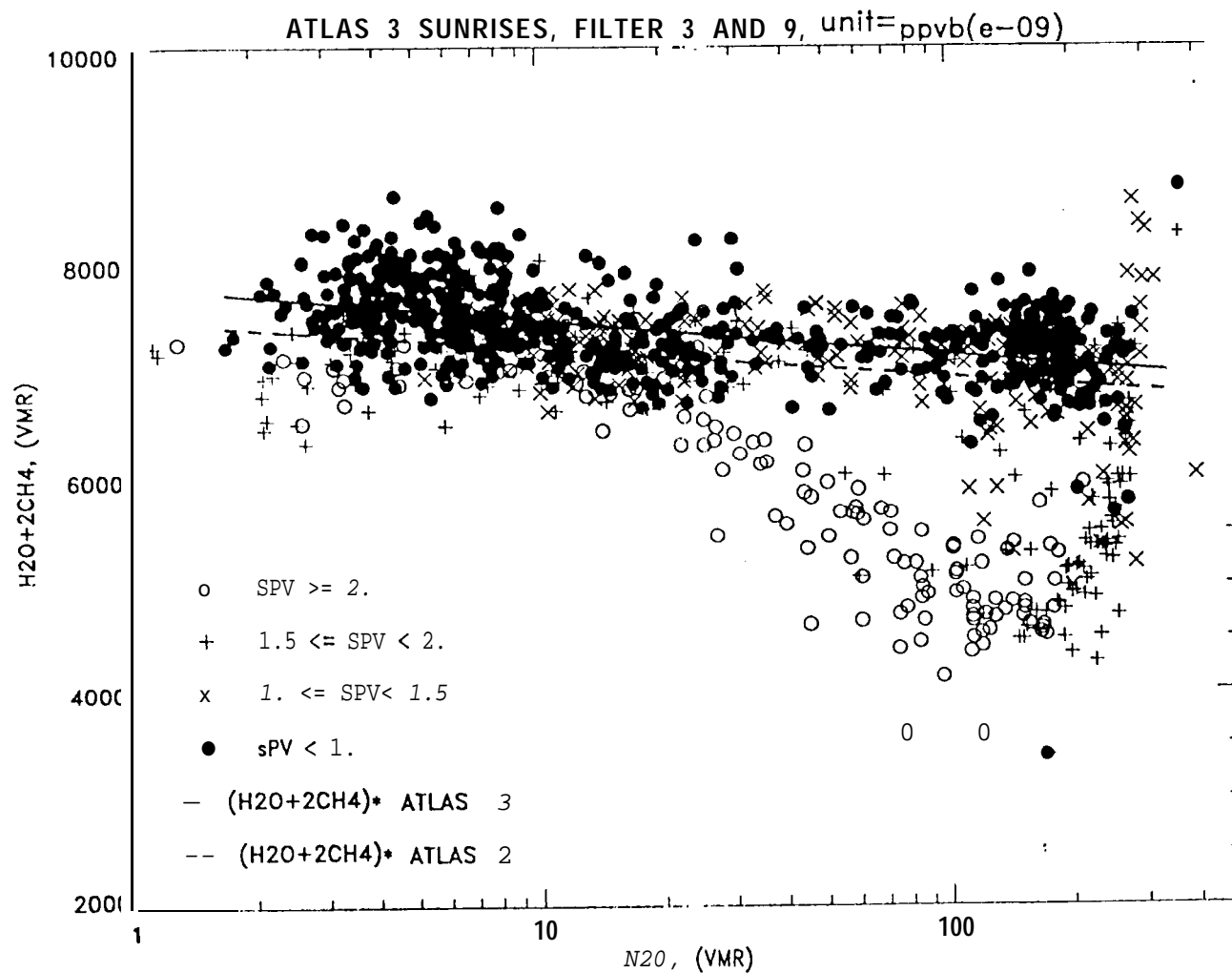


Figure 3

